High-resolution spectroscopy of atoms and molecules

New laser techniques, pulsed and continuous, which make it possible to see optical spectra without Doppler broadening, to label energy levels, and to enhance sensitivity, are now opening new applications.

Theodor W. Hänsch

Lasers are rejuvenating, even revolutionizing, the field of spectroscopy of atoms and molecules. Compared with the light of conventional sources, laser light is more—sometimes dramatically more—powerful, directional, spectrally pure and coherent. Laser light can be generated in extremely short pulses. Furthermore, tunable lasers can operate at wavelengths at which intense conventional sources such as spectral lamps simply have not been available. Lasers thus can enormously enhance the sensitivity and application range of classical spectroscopic methods, such as absorption spectroscopy, fluorescence spectroscopy and Raman spectroscopy.

At the same time, lasers have made it possible for us to observe new nonlinear spectroscopic phenomena. Intense laser light can change level populations and bleach absorbing transitions. The polarizabilities and dielectric susceptibilities of atoms or molecules themselves become functions of the light's field strength, and we encounter such effects as two-photon and multiphoton transitions, the generation of new light at the sum or difference frequency of the incident waves and stimulated light scattering. Laser light can prepare atoms effectively in coherent superpositions of quantum states, and it can give rise to fascinating coherent transient phenomena.

These effects are not only interesting in their own right and deepening our understanding of the nature of light and its interactions with matter, but some of them can be harnessed in nonlinear spectroscopic techniques to provide us with powerful new experimental tools. They allow us to probe the structure of atoms and molecules with an unprecedented depth of scrutiny.

The various ways in which lasers have already been used for atomic and molecular spectroscopy are much too numerous even to list here. Although several good reviews have been written[1,2] new and sometimes surprising results are being reported at an almost breathtaking pace. In this article I shall only attempt to look at some recent progress in one class of nonlinear spectroscopic techniques in which lasers have been particularly successful: high-resolution spectroscopy without the *Doppler broadening* that so often blurs important details in the spectra of free atoms and molecules.

Although some methods of Doppler-free laser spectroscopy have been known and used for more than a decade, numerous new approaches have been developed or suggested in the past few years. These techniques not only permit us to study fine spectral structures in unprecedented detail; they are also providing important tools for precision metrology and for fundamental physics research. Some of the same methods can also be used also to simplify and unravel complex absorption spectra. To illustrate what can be done I should like to describe only a few examples, mostly chosen from the research carried out by my collaborators and me at Stanford University.

Spectra without Doppler broadening

Atoms or molecules in gases are relatively free and undisturbed, but their spectral lines appear spread out by the Doppler effect over a range of wavelengths (typically about 1 part in 10^5) because they are moving in all directions with high thermal velocities. Those atoms moving towards an observer appear to emit or absorb light at larger frequencies than those at rest; those receding emit or absorb at lower frequencies. The resulting Doppler broadening often masks spectral fine and hyperfine structure, although each individual atom still retains its typically much narrower natural linewidth.

In the oldest approach to eliminate Doppler broadening, a well collimated atomic beam is used to select just a group of atoms that move nearly perpendicularly to the observer's line of sight. Excitation of the atoms with a tunable laser can be used with great advantage in this method because such lasers can easily be monochromatic to one part in 10^8 or better, and rather spectacular results have recently been obtained in this way.[1,2] Nevertheless, atomic-beam spectroscopy has its limitations; it can, for instance, not be applied easily to rare or expensive substances or to atoms in short-lived excited states.

Doppler broadening has also been reduced by the cooling of a gas sample. Because the velocity spread diminishes only with the square root of the temperature and because of condensation, this approach tends to be much less effective. But it has recently been pointed out[3] that the radiation-pressure force exerted by intense resonant laser light could be used to reduce the thermal velocities of gas atoms very rapidly—within microseconds—to very low values, corresponding to temperatures of less than one kelvin.

Vladilen Letokhov has suggested[4] that very slow atoms be trapped and suspended in the nodes of a strong standing-wave light field. These stationary atoms could then be observed over extended periods of time, and their spectrum would be completely free of Doppler broadening. Radiation cooling and trapping could be combined for this purpose, although light shifts in the strong trapping field are likely to limit the resolution in this as yet untried scheme. (See the article by Letokhov on page 23.)

The high intensity of laser light fortunately makes it possible to eliminate Doppler broadening in gas samples without any need for cooling. Two entirely different approaches have so far been used very successfully:

- ▸ In saturation spectroscopy and polarization spectroscopy, a group of atoms in

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Theodor W. Hänsch is a professor of physics at Stanford University, Stanford, California.

Lasers in research

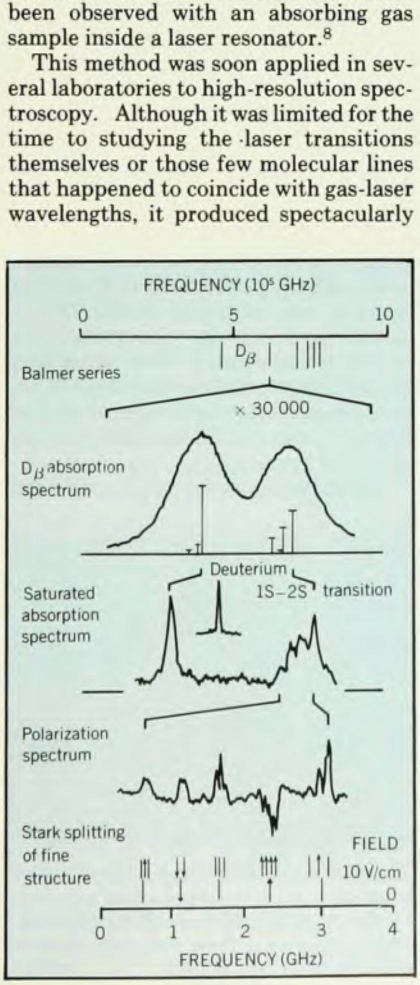
a narrow interval of axial velocities are "labelled" by their nonlinear interaction with a monochromatic travelling laser wave and a Doppler-free spectrum of these selected atoms is then observed, generally with a second laser beam as a probe.

▸ Two-photon excitation with two counterpropagating laser beams, so that the first-order Doppler shifts cancel, permits high-resolution spectroscopy of gases despite high thermal velocities.

Saturation spectroscopy

The first step towards saturation spectroscopy was the realization by Willis Lamb[5] that the two waves travelling in opposite directions inside a laser could work together to saturate the emission of those atoms that happen to have a zero component of velocity along the laser axis. Thus the power output would decrease when the laser length was adjusted to produce the light wavelength that would interact with those atoms. This "Lamb dip" was soon observed by R. A. Macfarlane, William Bennett Jr and Lamb[6] and independently by Abraham Szöke and Ali Javan.[7] "Inverse Lamb dips" have later been observed with an absorbing gas sample inside a laser resonator.[8]

This method was soon applied in several laboratories to high-resolution spectroscopy. Although it was limited for the time to studying the laser transitions themselves or those few molecular lines that happened to coincide with gas-laser wavelengths, it produced spectacularly narrow resonance lines. Through continuous refinements, John Hall and Christian Bordé[9] have recently been able to push the resolution of Lamb dips in methane, observed with a helium–neon laser near 3.39 microns, to about 2 parts in 10^{11}. They not only observed close molecular hyperfine splittings but also a line splitting due to the radiative recoil of the molecules that absorb or emit infrared photons.

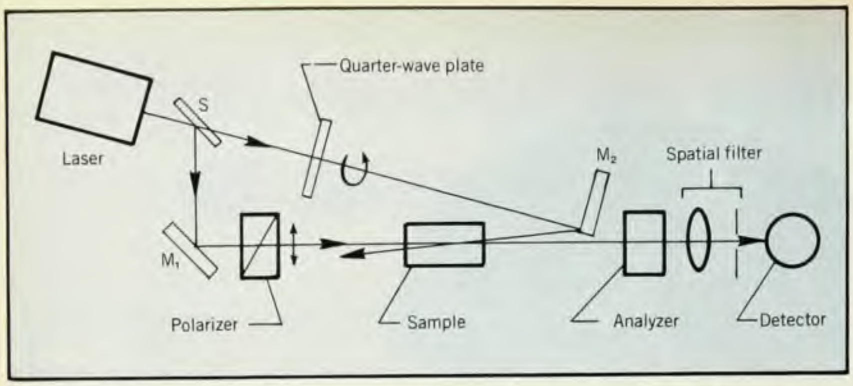


The blue Balmer beta line, as examined by various techniques. The **top** portions show the position of the line in the Balmer series and its Doppler-broadened absorption profile with theoretical fine structure. A saturation spectrum of the line, observed with a pulsed dye laser at 4860 Å, is in the **middle,** along with a two-photon spectrum of the 1S–2S transition, recorded simultaneously with the second harmonic of the same laser. Shown at the **bottom** is a polarization spectrum of a portion of the line, recorded with a cw dye laser. The Stark splitting of single fine-structure components is resolved; for comparison, the strongest theoretical Stark components for a 10-volt/cm axial field are shown below. The arrows indicate "crossover" resonances appearing half way between lines with a common upper (↑) or lower level (↓). Figure 1

Lamb-dip-stabilized gas lasers have become invaluable tools for precision metrology. They not only have established new *de facto* standards of length, but they have opened the way for new precision measurements of fundamental constants, and for stringent new tests of special relativity and of quantum electrodynamics as well.

A particularly sensitive and simple method of saturated absorption spectroscopy is one that was first used in 1970 by Bordé in Paris[10] and independently at Stanford,[11] following earlier related experiments at Heidelberg.[12] The absorbing gas sample is contained in a cell outside the laser resonator. A beam splitter divides the laser output into a strong saturating beam and a weaker probe beam, which are sent by mirrors in nearly opposite directions through the absorber. When the saturating beam is on, it bleaches a path through the cell, and the probe signal is received more strongly at the detector. As the saturating beam is alternately stopped and transmitted by a chopper, the probe signal is modulated. That, however, happens only when the laser is tuned near the center of the Doppler-broadened absorption line, where both beams are interacting with the same atoms, those that are standing still or at most moving transversely to the laser-beam direction.

Other techniques of Doppler-free saturation spectroscopy have also been reported.[1,2] Particularly noteworthy is the method of observing the combined satu-



Apparatus for Doppler-free polarization spectroscopy. A circularly polarized beam from the pump laser orients the rotation axes of atoms in a narrow range of velocities. These atoms can be detected with high sensitivity by a counterpropagating probe beam because they change its polarization, causing light to pass through the analyzer into the detector. Figure 2

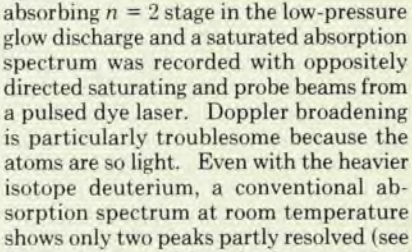
ration by two counterpropagating laser beams in the fluorescent sidelight rather than in absorption, as first demonstrated by Charles Freed and Javan.[13] Very dilute samples of negligible absorption can be studied in this way, in particular if the sensitivity is increased by chopping the laser beams at two different frequencies and by monitoring the modulation of the fluorescence at the sum or difference frequency, as reported by Arthur Schawlow and Michael Sorem.[14] The narrow-band spectrum of a selected group of molecules can also be observed by probing the dispersive refractive index rather than the absorption, as Bordé demonstrated with a gas sample inside a ring interferometer.[15]

All these methods were first used with gas lasers of very limited tuning range. Although broadly tunable visible lasers, especially dye lasers, began to become available about the same time, they generally did not produce sufficiently narrow spectral lines. But in late 1970 it was demonstrated at Stanford that linewidths as narrow as 300 MHz (5 parts in 10^7) can be produced by a pulsed dye laser pumped by a nitrogen laser when a beam-expanding telescope and an etalon were introduced inside the resonator.[16] Further narrowing could be obtained as needed by a confocal interferometer used as a passive filter. Continuous-wave dye lasers with linewidths much less than 1 MHz have become available as well.[17] But pulsed dye lasers continue to be useful for high-resolution spectroscopy, because they span a much wider conveniently accessible wavelength range and because their high peak power makes it possible to produce tunable ultraviolet or infrared radiation efficiently by nonlinear frequency mixing in crystals and gases.

Such a pulsed laser and the external saturation method made it possible to observe, for the first time, Doppler-free optical spectra of the simplest of all stable atoms, hydrogen.[18] As is well known, hydrogen has been intensively studied by spectroscopists for almost a century, because its simplicity permits detailed and accurate comparison with theoretical models.

The red Balmer alpha line ($n = 2$ to 3) of hydrogen and deuterium was studied in the initial experiment.[18,19] Subsequently, Sui Au Lee and her co-workers[20] observed the second member of the Balmer series, the blue Balmer beta line ($n = 2$ to 4), by the same technique; the results obtained for deuterium are illustrated in figure 1. The atoms were excited to the absorbing $n = 2$ stage in the low-pressure glow discharge and a saturated absorption spectrum was recorded with oppositely directed saturating and probe beams from a pulsed dye laser. Doppler broadening is particularly troublesome because the atoms are so light. Even with the heavier isotope deuterium, a conventional absorption spectrum at room temperature shows only two peaks partly resolved (see figure 1, top) although theory and rf studies agree on the underlying fine structure indicated. The saturation spectrum shown in the center of the figure gives a much clearer indication of the fine structure, but it still falls short of being completely resolved.

The earlier saturation spectra of the red Balmer alpha line were actually better resolved, and revealed—for the first time—single fine-structure components. The $n = 2$ Lamb shift could be clearly observed in the optical spectrum. More interesting than the splittings, measured previously by rf techniques, are the absolute wavelengths of the isolated components. An accurate measurement of the Balmer alpha wavelengths yielded the new value of the Rydberg constant with about ten times higher accuracy than had previously been possible.[19]



In two-photon spectroscopy without Doppler broadening, gas atoms in a standing-wave field are excited by absorbing two photons from opposite directions. Their first-order Doppler shifts are equal and opposite. Figure 3

The blue Balmer beta line is more difficult to observe because the fine structure splitting of the upper level is smaller. In addition, this line is more susceptible to splitting by the electric field in the discharge tube. It is also weaker and so requires stronger discharge current and a more intense saturating laser beam for a good signal, resulting in additional line broadening.

The spectrum was nonetheless good enough to serve as reference line for the first measurement of the hydrogen 1S ground-state Lamb shift. As discussed below this was done by comparing its wavelength with that of the 1S–2S two-photon transition, which was simultaneously observed with the frequency-doubled dye laser output. But it clearly seemed worthwhile to try to improve the resolution of the Balmer beta spectrum.

Polarization spectroscopy

This goal led to the development of "polarization spectroscopy," a sensitive new method of Doppler-free laser spectroscopy.[21] It is related to the saturated-absorption method, but the nonlinear interaction of the two counterpropagating laser beams is monitored *via* changes in light polarization instead of intensity. As shown in the scheme of figure 2, the saturating beam is circularly polarized. This beam labels atoms of selected axial velocity by orienting them through optical pumping. Normally, atoms in a gas have their rotation axes distributed at random in all directions. Because the absorption cross section for circularly polarized light generally depends on the atomic orientation, the saturating beam will preferentially deplete atoms with particular orientations, leaving the remaining ones polarized. Those atoms can then be detected with high sensitivity because they can change the polarization of a probe beam.

The linearly polarized probe light can be thought of as a combination of right-handed and left-handed circularly polarized waves of equal intensity. If the laser is tuned to the center of the Doppler-broadened line, where the probe beam sees the atoms polarized by the pump beam, more of the left-handed wave, say, is then absorbed than of the right-handed one, and the light passing through the sample becomes elliptically polarized. In addition, the polarization

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axis is rotated, because the two waves also see different refractive indices. The probe beam thus acquires a component that can pass through a crossed polarizer, which otherwise blocks the beam from the detector.

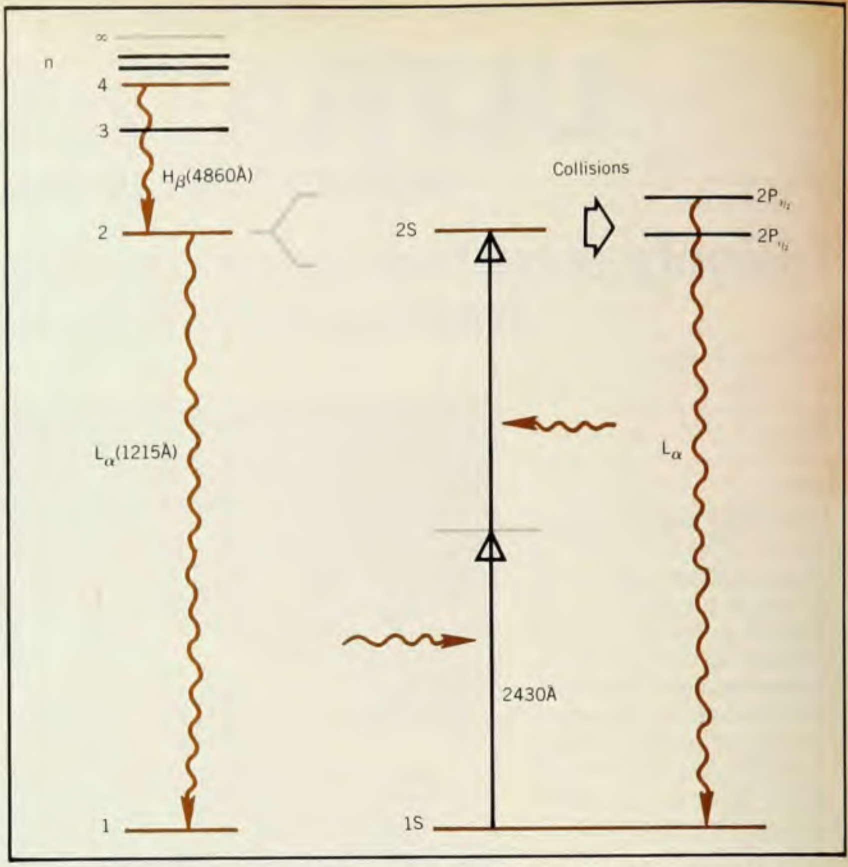
Polarization spectroscopy has an important advantage in its signal-to-noise ratio. There is almost no transmission of the probe beam until its polarization is changed by the atoms pumped by the saturating beam. With essentially no background, the signal is not easily obscured by noise or intensity fluctuations of the laser. This method can thus easily be used with fewer atoms and lower laser power.

For very small signals it is actually advantageous to uncross the polarizers slightly. The detector will then register some finite background, but the signal caused by saturated dispersion can now interfere with this background. Dependent on the sign of the dispersive polarization rotation, the intensity at the detector can either increase or decrease. Such a dispersive resonance line can be very useful for locking the laser frequency to an absorption line. It can be electronically differentiated to give a resonance peak of width less than half the natural linewidth.

The improved resolution obtained in this way for the hydrogen Balmer beta line can be seen in the lower part of figure 1. The shown portion of the spectrum corresponds to the cluster of lines at the right-hand side of the saturated absorption spectrum in this figure. The high sensitivity of polarization spectroscopy has made it possible to work with a highly monochromatic cw dye laser of low power. It has also been possible to operate with a very mild glow discharge with only few hydrogen atoms (1–2% absorption). Not only are the fine-structure lines and crossover lines much better resolved, but even the Stark splittings are clear enough to permit measurement of the electric field on the axis of the discharge tube. (As in saturated absorption spectroscopy, additional "crossover lines" are observed between any two resonant lines that share a common upper or lower level.)

The line components originating in the short-lived 2P state and in the metastable 2S state clearly have different widths. The narrowest observed linewidth so far has been about 25 MHz, but it may be possible to reduce the linewidth of the quasi-forbidden 2S–4S component (third line from the right) to as low as 1 MHz in the future.

Even the resolution of about 4 parts in 10^8, which has already been achieved, sets a new record for optical spectroscopy of this simplest of the stable atoms. It would certainly be possible to improve the accuracy of the Rydberg constant by another order of magnitude by carefully measuring the absolute wavelength of one of the resolved line components. If the isotope shift for hydrogen and deuterium (about 167 000 MHz) could be measured to better than 0.1 MHz, it could be used to confirm or improve the present value of the ratio of electron mass to proton mass. But it is expected that these quantities will soon be determined better by two-photon spectroscopy of the hydrogen 1S–2S transition. The Balmer beta spectrum remains nonetheless valuable as a reference for a measurement of the hydrogen ground-state Lamb shift.



A simplified level scheme for atomic hydrogen. Two-photon excitation of the metastable 2S state from the 1S ground state promises to yield extremely high resolution—ultimately higher than 1 part in 10^{15}. The excitation can be monitored by observing the collision-induced 2P-1S Lyman alpha fluorescence in the vacuum-ultraviolet spectral region. Figure 4

Two-photon spectroscopy

About three years ago, researchers in three different laboratories—at the University of Paris, at Harvard and at Stanford—demonstrated the feasibility of Doppler-free two-photon spectroscopy,[2] a particularly simple and elegant technique of high-resolution nonlinear laser spectroscopy. It has already been used widely for novel studies of atoms and molecules.

It has long been known that atoms can jump from the ground state to some excited level of the same parity by absorption of two photons that together provide the required energy, but experiments in the optical region have become possible only since the advent of strong laser sources. Two-photon spectroscopy has already become a valuable complement to single-photon spectroscopy because of its different selection rules, and because it permits one to reach high-lying states with longer wavelengths, which are often more readily generated and measured.

A particularly interesting situation arises if a gas sample is irradiated simultaneously with two monochromatic laser waves travelling in opposite directions. The atoms can then be excited by absorbing two counterpropagating photons, one from each beam, as diagrammed in figure 3.

As L. S. Vasilenko and his collaborators pointed out,[22] there is no net first-order Doppler effect in this case because, as seen from a moving atom, the two waves have equal and opposite Doppler shifts so that the sum frequency is constant, independent of the atomic velocity. (More generally, the net Doppler effect in multiphoton excitation vanishes if the momentum vectors of the participating photons add to zero.[23]) The two-photon excitation can often be observed with high sensitivity, for instance by monitoring the fluorescence light emitted by the excited atoms. All the atoms contribute to the

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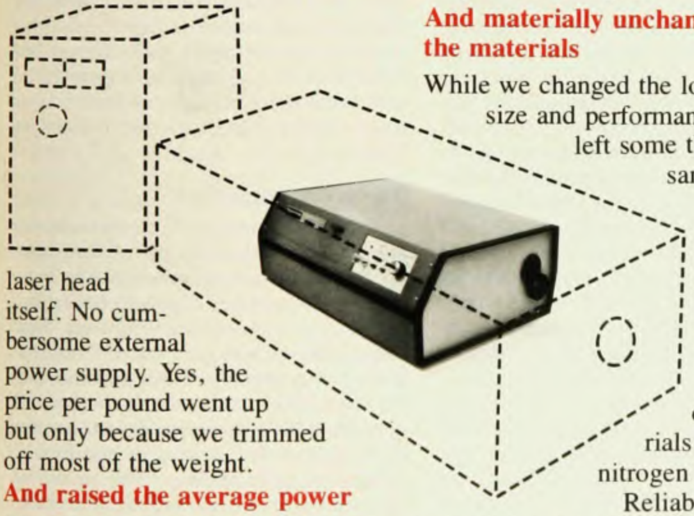

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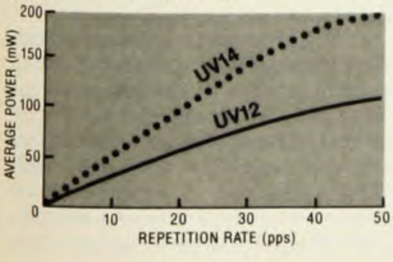

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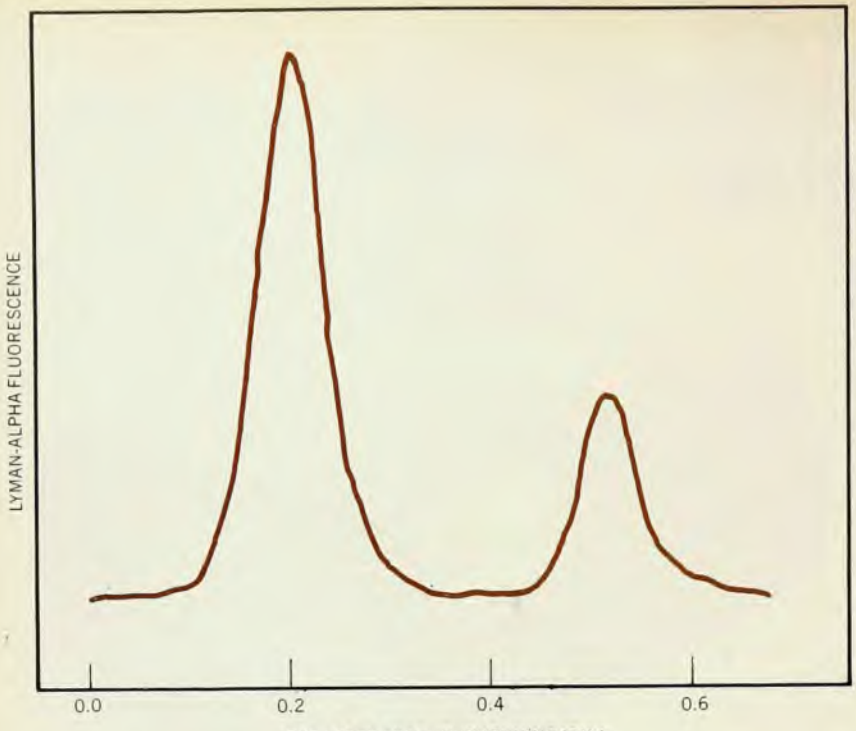


Doppler-free two-photon spectrum of the hydrogen 1S–2S transition, as recorded with a frequency-doubled cw dye-laser oscillator and a pulsed dye amplifier. Figure 5

resonant Doppler-free two-photon signal, not just a few with selected velocity, and a narrow resonance line is observed superimposed on the low, wide background produced by each beam separately.

After the new technique was first suggested, numerous authors have pointed out that a particularly interesting subject would be the transition from the 1S ground-state of atomic hydrogen to the metastable 2S state; see figure 4. If there are no external perturbations, the 2S state decays by spontaneous two-photon emission with a lifetime of about $\frac{1}{7}$ sec, and the natural linewidth should be on the order of only 1 Hertz. In principle, it should then be possible to achieve a resolution of better than 1 part in 10^{15} and to measure the line center to perhaps 1 part in 10^{17}.

In practice it will of course be extremely difficult to approach this ultimate resolution, because there are numerous possible causes of line broadening, including the second-order relativistic Doppler effect, light shifts in the intense laser field, transit time broadening and collision effects. But the main obstacle at present is the lack of a suitable strong, highly monochromatic laser at the required ultraviolet wavelength of 2430 Å. Photons at this wavelength can be generated readily by frequency doubling an intense pulsed dye laser beam at 4860 Å, but the linewidth can then not be narrower than the Fourier-transform limit (about 50 megahertz for the typical 10-nanosecond pulse length of a dye laser that is pumped by means of a nitrogen laser).

In initial experiments at Stanford it was possible to detect the Doppler-free two-photon resonance in atomic hydrogen in this way.[24] The ground-state hydrogen atoms were produced in a low-pressure gas discharge but observed outside the discharge plasma. After two-photon excitation, the metastable 2S atoms are induced by collisions to decay *via* fluorescence at the Lyman alpha line, which can be detected with high sensitivity. Figure 5 shows the 1S–2S two-photon spectrum for hydrogen, recorded very recently by Carl Wieman at Stanford with a somewhat improved laser. It combines a single-frequency cw dye-layer oscillator with a three-stage pulsed dye-laser amplifier, which permits the generation of several kilowatts peak power at the second-harmonic frequency. The resolution is close to the theoretical transform limit, and the $F = 1$–1 and 0–0 hyperfine components for hydrogen are fully resolved. For deuterium the $F = \frac{3}{2}$–$\frac{3}{2}$ and $\frac{1}{2}$–$\frac{1}{2}$ components are partially resolved.

Using earlier, somewhat less well resolved spectra, Lee and her associates were able to measure[20] the hydrogen–deuterium isotope shift to about 1 part in 10^4, improving earlier experimental values for the Lyman-alpha isotope shift by several orders of magnitude.

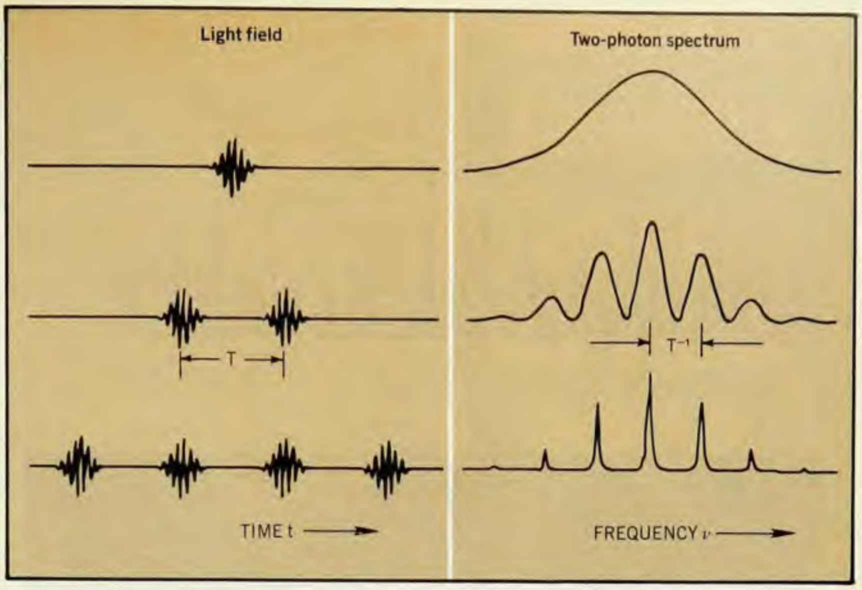
The same experiment yielded also, for the first time, an experimental value for the Lamb shift of the hydrogen 1S ground state, by comparing the 1S–2S two-photon spectrum with a saturated absorption spectrum of the Balmer beta line, which was simultaneously recorded with the fundamental dye-laser output, as discussed earlier. If Bohr's formula were correct, the latter $n = 2$–4 interval would be exactly equal to one-fourth the Lyman-alpha interval, and we would find the two resonances at exactly the same dye-laser frequency. The actual displacement is entirely caused by relativistic and quantum-electrodynamic corrections plus some small nuclear-structure effects. A precise measurement is a very sensitive test of the ground-state Lamb shift, which can not be observed by rf spectroscopy because there is no nearby P reference level. The accuracy of this first measurement was limited to about 1.5% by the relatively poor resolution of the Balmer beta line. New measurements, substituting the much superior polarization spectrum of the Balmer beta line, promise at least a tenfold improvement, and should also give first experimental evidence for an additional 23.4-MHz "Dirac shift" of the 1S state, which is caused by relativistic effects in the nuclear recoil. This effect can not be observed by rf spectroscopy, even for the excited levels, because it shifts all fine-structure levels of a given n by the same amount.

The resolution of even the best present hydrogen 1S–2S two-photon spectrum clearly falls far short of the ultimate limit and dramatic future improvements can be expected, which are likely to send the theorists back to their computers. Particularly promising in this context are some recently suggested or demonstrated new techniques of high-resolution laser spectroscopy that make use of multiple light fields.

Optical Ramsey fringes

The most obvious improvement for two-photon spectroscopy of hydrogen 1S–2S, which would overcome the Fourier-transform limit of pulsed laser spectroscopy, would be the use of a cw laser. Highly monochromatic cw radiation at 2430 Å has recently been generated at Stanford by summing the frequency of a blue krypton-ion laser and a yellow dye laser in a cooled crystal of ammonium dihydrogen phosphate. The power of about 0.1 mW may be sufficient for Doppler-free two-photon excitation of hydrogen 1S–2S if the beam is tightly focussed, but the short transit time of the atoms moving through the narrow beam waist would certainly cause considerable transit-time broadening.

A rather ingenious solution to this transit-time problem has recently been suggested by Ye. V. Baklanov and his collaborators.[25] An atomic beam could be sent through two consecutive transverse standing-wave light fields separated in space. After passing through the first field the atoms will be in a coherent superposition of states and will oscillate at the two-photon resonance frequency. The effect of the second light field depends on the phase of the radiation relative to the atomic oscillations, so that the atoms passing through this field will either be further excited or returned to the ground state by stimulated two-photon emission. When monitoring the net excitation by the two fields one should observe the optical analog of the well known Ramsey fringes, which are routinely utilized in rf spectroscopy of atomic beams.[26]



High spectral resolution is possible in two-photon spectroscopy with multiple short standing-wave light pulses. A single pulse produces a relatively broad, transform-limited spectrum (top); excitation with two sucessive light pulses can give rise to sinusoidal "optical Ramsey fringes" (center), and a train of pulses can produce narrow spectral lines (bottom). Figure 6

The spectral resolution is then limited by the travel time between the two fields rather than by the transit time through each waist. Doppler-free two-photon excitation with standing waves ensures that the fringe structure is not smeared out by dephasing due to the unavoidable small spread of transverse atomic velocities. Attempts to use these narrow spectral fringes for very-high-resolution spectroscopy of atomic beams are presently under preparation in several laboratories. (Similar optical Ramsey fringes have recently been observed by James Bergquist and his associates in saturated-absorption spectroscopy of a beam of fast neon atoms with spatially separated laser fields.[27])

To an atom traversing the separated field regions, the laser field appears as a succession of light pulses. This suggests that optical Ramsey fringes in two-photon excitation should also be observable with a pulsed laser source, without the need for an atomic beam, if a gas cell is irradiated by two standing-wave light pulses separated by a delay time T.

Although a single pulse produces a broad spectrum, as shown at the top of figure 6, two sequential pulses give rise to sinusoidal fringes (center) if the pulse delay T is scanned together with the light wavelength. The spacing between neighboring fringes is equal to the reciprocal of the pulse separation. Such interference fringes have recently indeed been observed by Michael Salour and Claude Cohen-Tannoudji,[28] who excited the sodium 3s–4d transition with two standing-wave dye-laser pulses produced with an optical delay line. The observation of spectral fringes of a width well below the Fourier-transform limit of an individual laser pulse opens new prospects for high-resolution spectroscopy, although the sinusoidal fringe structure would make it rather difficult to resolve spectral line components that are closely spaced.

These two-field excitation experiments can be regarded as spectral analogs to wave diffraction at a double slit. This analogy immediately suggests an important next step. If two-photon transitions are excited with a whole train of phase-coherent light pulses, as shown at the bottom of figure 6, the spectral fringes should condense into narrow lines, which, in the analogy, can be compared to the diffraction orders of a multislit aperture or grating.

Such narrow multipulse resonance lines have recently been observed by Richard Teets and his co-workers for the 3s–5s transition of atomic sodium with a very simple experimental setup.[29] The pulse train is produced by injecting a single short dye-laser pulse into an optical cavity formed by two mirrors. The gas sample is placed near one end-mirror so that the atoms see a pulsed standing-wave field once during each round trip, when the pulse is being reflected by the mirror. For spectral fine tuning the resonator length is scanned with a piezotranslator. The observed sharp multipulse interference fringes can be interpreted in terms of the modes of the optical resonator. The resolution is limited only by the natural atomic linewidth and by the losses of the resonator, not by the laser bandwidth.

The same scheme can provide a dramatic signal increase if the laser pulse is injected into the resonator without loss, for instance with some acousto-optic light switch. As long as atomic relaxation can be neglected, the probability of two-photon excitation for small intensities is proportional to the square of the number of pulse roundtrips; if the pulse recurs a hundred times, the two-photon signal will be 10^4 times stronger than in a single-pulse experiment. This enhancement can make it possible to use larger, less intense beams, reducing light shifts and transit-time broadening.

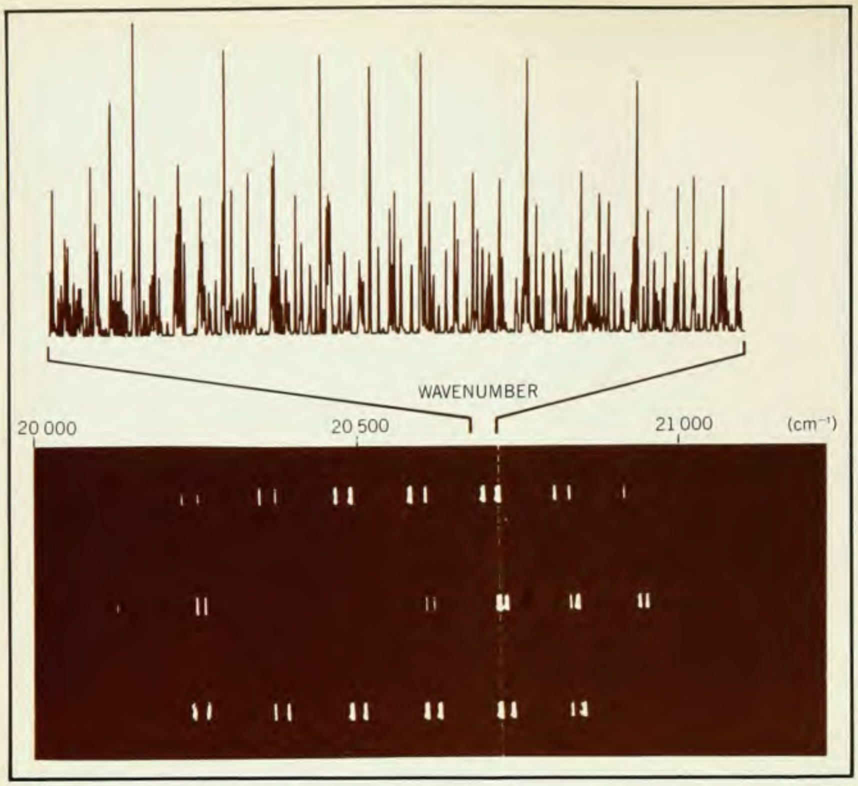
Two-photon excitation with multiple light pulses promises to extend the range of Doppler-free laser spectroscopy to new wavelength regions, in particular the ultraviolet and vacuum ultraviolet, where only short-pulse laser sources are available at present.

Polarization labelling of spectra

We have illustrated how nonlinear laser spectroscopy can provide a "microscope" to study the finest spectral details in high resolution, free of Doppler broadening. This ability has opened numerous new possibilities for interesting and fundamental research, even if we restrict our attention to the simplest atom. Naturally, a much richer field lies ahead if we include more complex atoms and molecules—studies of more complex aggregations of matter have in the past revealed surprising and important new effects that were not at all obvious from the basic laws of quantum mechanics. But for some of the more complex atoms and molecules even the coarse features of their absorption spectra are far from understood, and some means of classifying and unravelling these features can often be more important than the ability to see fine details.

It is quite remarkable that some of the same methods of nonlinear high-resolution laser spectroscopy can also be used to simplify atomic and molecular spectra and to unravel their complexities. Polarization spectroscopy can be a particularly powerful tool for this purpose, as demonstrated in recent experiments by Teets and others at Stanford.[30]

One of the difficulties in analyzing a complicated spectrum is that spectral lines from unrelated levels can occur at nearly the same wavelength. Even the absorption spectrum of a simple diatomic molecule such as Na_2 is greatly complicated by these accidental coincidences and near-coincidences, as the upper part of figure 7 indicates.



A small portion of the visible absorption spectrum of diatomic sodium molecules, shown at the top, is compared with spectra simplified by polarization labelling, bottom. Figure 7

At ordinary temperatures, numerous vibrational and rotational energy levels are populated in the electronic ground state. Each such level can absorb light at many different wavelengths, forming a series of doublets or triplets of spectral lines. The individual lines in such a group are those in which the rotational quantum number, J, of the upper, electronically excited state, differs from that of the lower state by -1, 0 or 1, according to the selection rules for dipole transitions.

The absorption spectrum would obviously be dramatically simplified if only a single lower state were populated. For the lowest levels such a situation can sometimes be approximated by the cooling of a gas through rapid expansion during flow through a supersonic nozzle. But this approach does not help one in identifying and studying the absorption lines that originate in the higher levels. Mark Kaminsky and his co-workers[31] have demonstrated recently that laser light can be used to "label" any selected lower level and to identify its absorption lines. The population of the chosen level is depleted by saturating a selected absorption line with a tunable laser, and a second probe laser beam identifies all lines with the same lower state by their weakened absorption. Much higher sensitivity has been achieved subsequently by combining this method of lower-level labelling with the technique of polarization spectroscopy so as to provide a simplified spectrum that can be seen or photographed.

The apparatus for polarization labelling is shown in figure 8. For convenience, nitrogen-pumped dye lasers were used both for labelling of a chosen level and for probing. The pumping laser is monochromatic and can be circularly or linearly polarized. The probe is a broad-band laser with a continuous output spectrum 300 Å wide. Crossed polarizers are placed into the probe beam, in front of and behind the absorption cell. The polarized pump-laser beam then selectively removes molecules that happen to be oriented so as to absorb it, leaving the remaining ones in that level with a complementary alignment. Thus the gas (Na_2 in these preliminary experiments) can change the polarization of the probe at the wavelengths of all absorption lines from the polarized level. Those wavelengths can then pass through the crossed analyzer and appear as bright lines on a dark background in a photograph of the spectrum.

In the spectrum in the lower part of figure 7, the probe-laser wavelengths extend on either side of a pump at about 4830 Å and cover transitions to the low vibrational states of the B band $B^1\Pi_u \leftarrow X^1\Sigma_g^+$ of the diatomic sodium molecule. As the pump wavelength is shifted very slightly, different lower levels are polarized and the various spectra are observed. These spectra resemble those from laser-excited fluorescence, but they reveal all absorption lines with a common lower state rather than emission lines with a common upper state. They can provide direct information about the spectroscopic constants and quantum numbers of the excited state. The vibrational quantum numbers can, for instance, immediately be inferred from figure 7 by simply counting down until the doublets end at $v' = 0$. Any irregularity in the series of doublets can reveal perturbations by neighboring triplet states, which would be very difficult to discover in the forest of lines of the ordinary absorption spectrum.

Collision processes in the presence of buffer gas produce a series of satellite lines around each doublet. These originate from ground-state levels close to the pumped level, and differ from it by 2,4,6, . . . units of the rotational quantum number. They indicate that collisions change the magnitude of the angular momentum without destroying the orientation of the molecules.

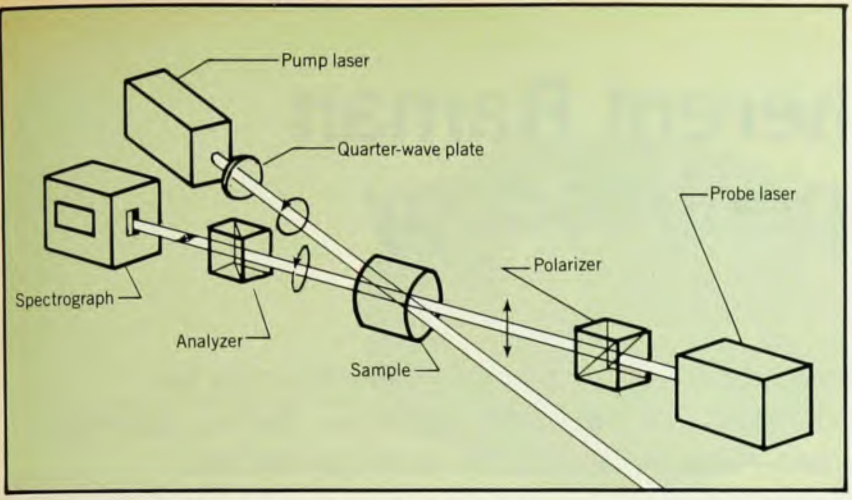
It is also possible to pump a line of one band while observing some other band. For example, one could pump a transition in the infrared, where the spectroscopic constants are often well known, and probe a transition in the ultraviolet.

Once the spectral lines are identified by polarization labelling, their wavelengths can obviously be measured with very high precision. If highly monochromatic tunable dye lasers are used for pumping and probing, the polarization spectrum is free of Doppler broadening, as we have seen before. With accurate, fringe-counting digital wavelength meters it is thus easily possible to determine much-improved spectroscopic parameters, even for molecules that were studied as thoroughly in the past as diatomic sodium.

New territory

The few examples illustrate how nonlinear laser spectroscopy of atoms and molecules makes it now possible to explore new territory and to gather information that would be difficult or impossible to determine by classical spectroscopic methods.

I have not mentioned many other interesting recent applications of laser spectroscopy, such as studies of atoms in high Rydberg states or in highly excited autoionizing states. Nor have we been able to discuss other interesting laser techniques, such as methods of ultrasensitive spectroscopy, which are providing analytic tools of unprecedented power. (Trace absorptions can be detected sensitively by placing the absorber inside a dye laser cavity, or by monitoring the sound generated by absorption of modulated laser light. Fluorescence spectroscopy with lasers has been carried to densities of less than one atom, on the average, in the beam, and single atoms or



To unravel complex absorption spectra by polarization labelling, a monochromatic circularly polarized laser beam is used in this apparatus to orient molecules in one selected lower level. The gas then changes the polarization of a broad-band beam from a probe laser at all wavelengths that correspond to absorption lines from this level. Figure 8

molecules in selected quantum states can be detected among 10^{19} background molecules through resonant multi-step photoionization.)

The high sensitivity and resolution of laser techniques has stimulated interesting new approaches to challenging problems in fundamental physics, such as the detection of parity-violating neutral-current effects in atoms or molecules, or the search for quarks and other elusive species, or new sensitive tests to reveal "ether drifts" that might cause a directional anisotropy of the velocity of light.

We do not have to be overly optimistic to expect a rich harvest of new results—and perhaps surprising discoveries—from the new techniques in the future, and physics, chemistry and biology will surely be among the sciences to benefit.

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